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Title: **SIMULTANEOUS VAPORIZATION AND IONIZATION
SPECTROMETRY SOURCE, AND ACCOMPANYING
SPECTROMETER; METHOD FOR SIMULTANEOUS VAPORIZATION
AND IONIZATION OF SAMPLE PARTICULATE TO PRODUCE
ANALYTE IONS**

Inventors: **David A. Atkinson
Paul Mottishaw**

1 **SIMULTANEOUS VAPORIZATION AND IONIZATION SPECTROMETRY**
2 **SOURCE, AND ACCOMPANYING SPECTROMETER; METHOD FOR**
3 **SIMULTANEOUS VAPORIZATION AND IONIZATION OF SAMPLE**
4 **PARTICULATE TO PRODUCE ANALYTE IONS**

5
6 **CONTRACTUAL ORIGIN OF THE INVENTION**

7 This invention was made with United States Government support under Contract
8 No. DE-AC07-94ID13223, now Contract No. DE-AC07-99ID13727 awarded by the
9 United States Department of Energy. The United States Government has certain rights in
10 the invention.
11

12 **FIELD OF THE INVENTION**

13 This invention pertains to methods and apparatus for spectrometric analysis of a
14 sample, and more particularly to a method and apparatus for the simultaneous
15 vaporization and ionization of a sample to be analyzed using a spectrometer. In one
16 aspect, the invention comprises an ion mobility spectrometer or an atmospheric pressure
17 mass spectrometer.
18

19 **BACKGROUND OF THE INVENTION**

20 The modern practice of ion mobility spectrometry (IMS) normally involves
21 ionization processes centered on the use of a radioactive ^{63}Ni or ^3H source, typically foil.
22 Aside from the fact that the radioactive source has logistical problems in documenting

1 control and safety of the source, including licensing issues and transport of apparatus
2 using the radioactive source into foreign countries, this type of ionization device relies
3 upon gas phase processes to effect ionization. Therefore, particulate matter is analyzed
4 after a transfer of analyte ions from the particulate to the gas phase, typically by thermal
5 desorption/vaporization, as is the current popular practice.

6 Another drawback to the current technology in ion mobility spectrometry (IMS)
7 and atmospheric pressure ionization (API) mass spectrometry is that typically the sample
8 particulate needs to be vaporized before introduction into an ionization source, leading to
9 potential thermal degradation of analyte ions and increased instrument complexity in the
10 way of controls and space requirements for both ionization and vaporization elements. In
11 addition, IMS instruments require that an ion gate be placed in front of the drift tube in
12 the spectrometry analyzer to control the flow of ions into the drift tube. Ion gates are
13 fragile and, thus, affect the ruggedness of an instrument containing such a device.
14 Additionally, ion gates require the addition of complex electronics to drive gate pulses,
15 increasing the cost of IMS instruments.

16 Since the resurgence of IMS as a technique for field use for applications such as
17 the detection of explosives and other contraband in airports, there has been an increased
18 need to have an inexpensive, robust IMS apparatus available for such use. It is also
19 desirable to have a atmospheric pressure ionization mass spectrometer which does not
20 rely on thermal desorption/vaporization prior to the introduction of analyte ions to the
21 detector.

1 The use of an electrospray device in mass spectrometry is known as a means for
2 ionizing and vaporizing a sample prior to introduction into the spectrometry analysis
3 section, but such use is limited to mass spectrometers which operate under a vacuum.
4 Further, the liquid transfer medium for carrying the sample into the electrospray device
5 presents a substantially different system than the gas carrier fluid systems used in IMS
6 and API spectrometry.

7 Therefore, what is needed is a rugged, efficient, non-radioactive method and
8 apparatus for vaporizing and ionizing sample particulate in IMS and API spectrometers.

9 10 **SUMMARY OF THE INVENTION**

11 A first aspect of the invention includes a simultaneous vaporization and ionization
12 spectrometry source. The source has an electrically conductive conduit configured to
13 receive sample particulate carried by a carrier fluid stream, the conduit having a discharge
14 end with an opening configured to discharge the sample into a spectrometry analyzer.

15 The source further includes an electrically conductive reference device positioned
16 proximate the discharge end of the conduit at a distance greater therefrom than the
17 Paschen distance.

18 A second aspect of the invention includes a spectrometer having a spectrometry
19 analyzer and a simultaneous vaporization and ionization spectrometry source in
20 accordance with the first aspect of the invention.

21 The invention further includes methods for simultaneous vaporization and
22 ionization of sample particulate to produce analyte ions for spectrometric analysis. In a

1 third aspect of the invention, the method includes the steps of providing a particulate
2 sample to be spectrometrically analyzed, providing a first electrode, and providing a
3 second electrode proximate the first electrode. An electrical potential is maintained
4 between the first electrode and the second electrode such that an electrical potential exists
5 between the two electrodes. A carrier fluid is provided to transport the particulate sample
6 to a point proximate the first and second electrodes. Electrical arcing between the first
7 and second electrodes is caused at a time when the particulate sample arrives at the point
8 proximate the first and second electrodes to cause at least partial vaporization and
9 ionization of the particulate sample and thereby produce analyte ions, which can
10 thereafter be analyzed in a spectrometry analyzer.

11 In a fourth aspect of the invention, a method for simultaneous vaporization and
12 ionization of a particulate sample in accordance with the third aspect of the invention is
13 disclosed. However, in the fourth aspect the electrical potential at the first electrode and
14 the electrical potential at the second electrode are maintained at a point above an
15 electrical breakdown potential between the two electrodes, such that the arrival of the
16 particulate sample at the point proximate to the two electrodes causes a corona discharge
17 as a result of altering the breakdown potential. The corona discharge causes at least
18 partial vaporization and ionization of the particulate sample to produce analyte ions.
19

1 **BRIEF DESCRIPTION OF THE DRAWINGS**

2 Preferred embodiments of the invention are described below with reference to the
3 following accompanying drawings.

4 Fig. 1 is a schematic diagram showing a spectrometer which can use the
5 simultaneous vaporization and ionization source of the present invention and in which the
6 methods of the present invention can be carried out.

7 Fig. 2 is an isometric drawing of one embodiment of a simultaneous vaporization
8 and ionization spectrometry source in accordance with the present invention.

9 Fig. 3 is an exploded diagram of the spectrometry source of Fig. 1 shown in
10 isometric view.

11 Fig. 4 is a side elevation sectional view of the spectrometry source of Fig. 2.

12 Fig. 5 is a side elevation sectional view of an alternate embodiment of the
13 spectrometry source of Fig. 3.

14 Fig. 6 is an isometric diagram showing an alternate embodiment of the reference
15 device used in the present invention.

16 Fig. 7 is an isometric diagram showing an alternate configuration for the reference
17 device used in the present invention.

18
19 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

20 This disclosure of the invention is submitted in furtherance of the constitutional
21 purposes of the U.S. Patent Laws "to promote the progress of science and useful arts"
22 (Article 1, Section 8).

Turning to Fig. 1, a simplified block diagram of a spectrometer which can use the simultaneous vaporization and ionization spectrometry source of the present invention is shown. The methods of the present invention can also be practiced using such a spectrometer. The spectrometer includes a sample entry section 5 configured to suspend a sample in a carrier fluid. In applications such as IMS and API mass spectrometry, the carrier fluid is typically a gas. The spectrometer 1 further comprises an ionization and vaporization unit 10. Traditionally, such units include both a thermal desorption/vaporization component to vaporize the sample, as well as a separate unit for ionization of the vaporized sample. Following ionization, the ionized particles are drawn toward the spectrometry analyzer 20. Such is typically performed by applying an electric field to the analyzer to attract the ionized, charged particles. A sweep gas counter flows against the directional flow of the ionized particles to remove any neutral particles from the stream to prevent them from entering the drift tube of the analyzer 20.

Turning to Fig. 2, a first embodiment of the apparatus in accordance with the present invention is shown. The simultaneous vaporization and ionization spectrometry source 10 of Fig. 2 includes an electrically conductive conduit 104 and an electrically conductive reference device 106. A sample to be analyzed in the spectrometry analyzer is provided to the conduit 104 via the sample inlet 102. The sample is typically provided to the conduit by way of a carrier fluid which, in IMS and API spectrometry, typically comprises a gas. The sample is typically in the form of particulate in the gas stream.

The electrically conductive conduit 104 may alternately be known as the sample outlet or the first electrode. A first electrical potential is applied to the conduit 104 by

1 way of an electrical contact or connector 114. A second electrical potential is applied to
2 the electrically conductive reference device 106 by way of the electrical contact or
3 connector 116. The conduit 104 and the reference device 106 are electrically isolated
4 such that current does not flow between these two components. The electrically
5 conductive reference device 106 preferably further includes a discharge portion 110
6 which is located proximate, but not in contact with, the conduit 104. More preferably, the
7 discharge portion 110 is located a distance from the conduit greater than the Paschen
8 distance, being the distance at which an electrical potential between two items cannot be
9 maintained. The Paschen distance will vary according to atmospheric pressure,
10 atmospheric temperature, humidity, the electrical potential between the two electrodes,
11 the type of carrier gas used, and other factors. Since many of these factors are typically
12 known or can be measured, it is typically possible to calculate the Paschen distance with
13 some accuracy. A margin of safety can also be provided to account for variances in these
14 variables.

15 Turning to Fig. 3, an exploded isometric diagram of the apparatus 10 of Fig. 2 is
16 shown. In the particular embodiment shown, it is seen that the sample inlet 102 and the
17 conduit 104 comprise separate components. The sample inlet 102 is further comprised of
18 instrument tubing components 120, 122 and 124. The sample inlet 102 and the conduit
19 104 are fitted to body 101 which is preferably manufactured from an electrically
20 insulating material. The reference device 106 is provided with a plurality of openings or
21 holes 112 which allow sweep gas to pass from the ionization area into the channel 138

1 where the gas is then removed at the sweep gas outlet line 118 by way of sweep gas outlet
2 path 142 (see Fig. 4).

3 Turning to Fig. 4, a side sectional elevation view of the first embodiment of the
4 apparatus 10 shown in Fig. 2 is shown. In the embodiment shown, conduit 104 is
5 threaded into the body 101, and sample inlet section 102 is threaded into the other end of
6 the body 101. The sample inlet 102 and conduit 104 are separated by a region 140, thus
7 electrically isolating the conduit 104 from the sample inlet 102. This is done since an
8 electrical potential is provided to conduit 104 by contact 114 and it is, therefore,
9 preferable to electrically isolate the sample inlet 102 to prevent accidental disruption of
10 the electrical potential established between the conduit 104 and the reference device 106.

11 Fig. 4 also shows the manner in which the first electrical contact 114 and the
12 second electrical contact 116 are inserted into the body 101 in order to contact the conduit
13 104 and the reference device 106, respectively.

14 Returning to Fig. 3, it is seen that the first electrical contact 114 comprises an
15 electrical connector 126 which is sheathed by an electrical insulator 128. Securing
16 devices 129 (here, nuts) are used to secure an electrical source to the first contact. In a
17 like manner, the second contact 116 comprises an electrical connector 130, an insulating
18 sheath 132, and securing devices 134 (here, nuts) to attach an electrical source to the
19 contact. Note that an electrical ground wire can also be connected to contact 114 or 116
20 as opposed to an electrical source.

21 Referring again to Fig. 4, the holes 112 in the reference device 106 allowing
22 sweep gas to pass into the annular space 138 and out through the sweep gas exit port 142

1 and outlet line 118 are clearly shown. Sweep gas moves in the direction indicated by
2 arrows B, whereas the ionized particles move in the direction indicated by arrows A
3 towards the spectrometry analyzer 20. Because of the polarity typically applied to the
4 spectrometry analyzer 20 in order to attract ionized analyte into the drift tube, in the
5 preferred embodiment a positive voltage is applied to the electrical contact 116 and,
6 hence, the reference device 106. Consequently, a ground potential is applied to the
7 electrical contact 114, and hence, the conduit 104. In one embodiment, the electrical
8 potential between the conduit and the reference device is at least ten volts. More
9 preferably, the electrical potential between the conduit and the reference device is less
10 than about 250 volts.

11 The apparatus can further be provided with a ballast resistor 169 and a voltage
12 controller 170 as shown in Fig. 4. The ballast resistor can provide a current limitation in
13 an arc generated during operation of apparatus 10. Such can assist in controlling the arc,
14 and in protecting the voltage controller from a "dead short" scenario during arcing.
15 Although ballast resistor 169 is shown to be external and separate from voltage controller
16 170, it is to be understood that ballast resistor 169 could also be provided as a component
17 of voltage controller 170.

18 The voltage controller can be a programable device and can be configured to
19 allow the electrical potential between the conduit and the reference device to be
20 selectively determined. The voltage controller can be further provided with
21 instrumentation (not shown) to measure conditions which can affect the Paschen distance.
22 Based on these measurements and calculations made by a processor within the voltage

1 controller, the electrical potential between the conduit and the reference device can be
2 varied using the voltage controller. The voltage controller can also be a manually
3 adjustable unit allowing an operator to selectively establish the potential between the
4 conduit 104 and reference device 106.

5 The reference device 106 shown in Fig. 4 comprises a flat metallic ring 108
6 having a probe or tip 110 connected thereto and positioned near the discharge end 156 of
7 the conduit 104. As discussed previously, the tip 160 of the probe 110 is maintained at a
8 distance greater than the Paschen distance from the conduit 104.

9 Turning to Fig. 5, an alternate embodiment of the invention is shown wherein the
10 reference device 106 of Fig. 4 has been replaced with reference device 148. Reference
11 device 148 comprises an electrical wire 150 having insulation 152 disposed thereabout.
12 In the embodiment shown, the reference device 148 is inserted through a small opening in
13 the sample inlet 102, which is then plugged with a plug 146. The reference device 148
14 passes along the conduit 104 until the end of the reference device is positioned near the
15 discharge end 156 of the conduit. The end of the reference device has the insulation
16 removed to expose a small piece of conductive metal 154 at the end of the conduit 104.
17 Again, the electrical contact 154 is positioned such that it is greater than the Paschen
18 distance from any surface of conduit 104. The embodiment shown in Fig. 5 is a
19 preferable configuration to that shown in Fig. 4 since the design shown in Fig. 5 projects
20 the ionized particles indicated by arrow A more efficiently towards the spectrometry
21 analyzer 20.

1 Preferably, the point of the reference device 106 or 148 nearest the conduit 104,
2 being the point at which electrical arcing will occur, is fabricated from a material selected
3 from the group consisting of stainless steel, gold, and platinum. Platinum is a preferred
4 material of construction for the end of the reference device where electrical arcing will
5 occur, as platinum tends to resist pitting due to electrical arcing.

6 In one embodiment, the conduit 104 comprises a hypodermic needle. Turning to
7 Fig. 6, an alternate embodiment of the invention is shown wherein the reference device
8 182 comprises a circular ring which is positioned between the conduit 106 and the
9 spectrometry analyzer 20. In Fig. 7, yet another embodiment is shown wherein the
10 reference device 184 comprises a metal grate which is positioned between the discharge
11 end 156 of conduit 106 and the spectrometry analyzer 20.

12 **Spectrometer:**

13
14 In addition to disclosing a simultaneous vaporization and ionization spectrometry
15 source, the invention includes a spectrometer including a ionization and vaporization
16 source in accordance with the above disclosure. The spectrometer generally comprises
17 those elements shown in Fig. 1, being a sample inlet section 5, an ionization vaporization
18 unit 10 in accordance with the above disclosure, and a spectrometry analyzer 20.

19 Preferably, the sample inlet portion 5 and the spectrometry analyzer 20 comprise
20 ionization mobility spectrometry components or atmospheric pressure ionization mass
21 spectrometry components. That is, the sample particulate is suspended in a carrier fluid
22 comprising a gas. Further, in each application, the spectrometry analyzer is operated at

1 ambient pressures rather than at a vacuum, as it typical in mass spectrometry. It is noted
2 that mass spectrometers are run at vacuum and IMS are run at ambient pressures. A
3 device of the present invention can operate at ambient for mass spectrometry by placing
4 the device outside of a vacuum, near a mass spectrometer, with a small orifice leading
5 into the mass spectrometer (at vacuum). Ions from the device can go through the orifice.

6 The spectrometer can further comprise the control unit 170 shown in Figs. 1 and 4
7 and described further herein, and can additionally comprise a ballast resistor 169
8 provided separately from the control unit or as a component of the control unit. The
9 voltage controller 170 can be a programmable voltage controller. Accordingly, the
10 voltage controller 170 can be programed to establish the electrical potential between the
11 conduit 104 and the reference device 106 at a voltage slightly less than the breakdown
12 potential between the two electrodes. The breakdown potential is the electrical potential
13 at which electrical arcing will occur between the two electrodes. This can be
14 accomplished by increasing the potential between the two electrodes until electrical
15 arcing occurs and thereafter, slightly reducing the electrical potential to establish the
16 voltage at a potential slightly less than the breakdown potential. When a sample
17 particulate arrives at the discharge end of the conduit 104, the particle will interfere with
18 the voltage equilibrium between the conduit 104 and the reference device 106 or 148,
19 causing electrical arcing to occur between the conduit 104 and the reference device. This
20 arcing will cause a corona effect which will simultaneously vaporize and ionize at least a
21 portion of the sample particulate, producing analyte ions which can then be analyzed in
22 the spectrometry analyzer 20.

1 The control unit 170 of Fig. 1 can also be configured to generate voltage pulses
2 between the conduit 104 and the reference device 106 or 148 to periodically create a
3 corona effect, rather than relying on the arrival of particulate matter at the discharge end
4 156 of the conduit. Such can be used when a large quantity of sample particulate is
5 anticipated which can cause a high incidence of arcing in the configuration described
6 above wherein the potential between the conduit and the reference device is established
7 slightly below the breakdown potential.

8 In a third embodiment, the control unit 170 of Fig. 1 can be configured to
9 establish the electrical potential between the conduit 104 and the reference device 106 or
10 148 such that there is continuous arcing or corona effect between the two electrodes.

11 In the embodiment described wherein the electrical potential is established to
12 occur on a periodic pulse, the spectrometer can be constructed without the need for an ion
13 gate between the ionization unit and the spectrometry analyzer 20.

14 15 **Method:**

16 The invention further includes methods for simultaneous vaporization and
17 ionization of sample particulate to produce analyte ions for spectrometric analysis. The
18 method includes the steps of providing a particulate sample to be spectrometrically
19 analyzed. Such can be accomplished in any of the traditional methods known for
20 providing a sample to an IMS or API mass spectrometer. The method further includes
21 the steps of providing a first electrode and providing a second electrode proximate the
22 first electrode. Referring to Fig. 4, the first and second electrodes are provided in the

1 form of the conduit 104 and the reference device 106, with no particular association as to
2 which of these two constitutes either the first or second electrode. At least a portion of
3 the two electrodes are provided in close proximity such that electrical arcing can occur
4 between the two electrodes when a sufficiently high electrical potential is applied there
5 between.

6 In the next step in the method, a first electrical potential is provided at the first
7 electrode and a second electrical potential is provided at the second electrode, such that
8 an electrical potential exists between the two electrodes. Either of the two electrical
9 potentials can consist of ground potential or a zero voltage potential. The other electrical
10 potential typically comprises a positive voltage such that a differential voltage is
11 established between the two electrodes. A carrier fluid is provided for transporting the
12 particular sample to a point proximate the first and second electrodes. In IMS and API
13 spectrometry, the carrier fluid typically comprises gas such as air or nitrogen. The
14 particulate sample provided is thus transported via the carrier fluid to a point proximate to
15 the first and second electrodes. The method further includes the step of causing electrical
16 arcing between the first and second electrodes at a time when the particulate sample
17 arrives at a point proximate thereto, to cause at least partial simultaneous vaporization
18 and ionization of the particulate sample and thereby produce analyte ions which can be
19 analyzed the spectrometry analyzer. Preferably, the method is practiced using an IMS or
20 an API mass spectrometer.

21 In a first variation of the method, the electrical potential between the first and
22 second electrodes is maintained slightly above the breakdown potential between the two

1 electrodes. Electrical arcing between the first and second electrodes is caused by the
2 arrival of the particulate sample at a point where the two electrodes are proximate to one
3 another. Arrival of the sample particulate at this point alters the breakdown potential
4 between the electrodes, resulting in a corona discharge which causes at least partial
5 simultaneous vaporization and ionization of the particulate sample and thereby produce
6 analyte ions.

7 Establishing the electrical potential between the first and second electrodes at a
8 point slightly below the breakdown potential can be accomplished by increasing the
9 potential between the two electrodes until a corona discharge occurs in the absence of
10 particulate sample at a point proximate to the first and second electrodes. The potential
11 between the two electrodes is then reduced slightly to create an equilibrium state between
12 the electrodes where no corona discharge occurs in the absence of sample particulate at a
13 point proximate to the two electrodes. Thereafter, the arrival of particulate sample at a
14 point proximate to the two electrodes will alter the breakdown potential, causing a corona
15 discharge and at least partial vaporization and ionization of the particulate sample. In this
16 variation, the potential between the two electrodes is established at between about 10 and
17 about 50 volts in the equilibrium state. It is noted, however, that the potential between
18 the two electrodes is condition dependent, and can vary depending on distance between
19 the electrodes, temperature, humidity and gas type, for example. Such variation can
20 change the potential to outside of the stated range between about 10 and about 50 volts.

21 In a second variation on the method, the electrical potential between the first and
22 second electrodes is maintained such as to produce a continuous arcing there between,

1 thereby causing continuous simultaneous vaporization and ionization of at least a portion
2 of the sample particulate passing through the corona.

3 In a third variation of the method, the electrical potential between the first and
4 second electrodes is initially maintained at a level below the breakdown potential
5 between the electrodes. The potential between the two electrodes is then periodically
6 increased to the point where a corona discharge between the electrodes occurs resulting in
7 at least partial simultaneous vaporization and ionization of any particulate sample which
8 happens to pass through the corona. In this manner, the flow of analyte ions to the
9 spectrometry analyzer can be controlled according to any preferred timing sequence by
10 the use of the control unit 170 of Fig. 1. Operating the spectrometer according to the
11 method and the third variation removes the need for an ion gate to be placed in front of
12 the spectrometry analyzer.

13 While the invention has been described particularly with respect to sample which
14 is in particulate form, it should be understood that the particle need not be a solid particle,
15 but can, in fact, comprise a droplet of entrained liquid in a gas stream of carrier fluid.

16 In compliance with the statute, the invention has been described in language more
17 or less specific as to structural and methodical features. It is to be understood, however,
18 that the invention is not limited to the specific features shown and described, since the
19 means herein disclosed comprise preferred forms of putting the invention into effect. The
20 invention is, therefore, claimed in any of its forms or modifications within the proper
21 scope of the appended claims appropriately interpreted in accordance with the doctrine of
22 equivalents.